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ELECTROSYNTHESIS OF 5-CHLORO-2-(2,4 DICHLORO PHENOXY) BENZENAMINE USING TITANOUS/TITANIC REDOX MEDIATOR

P THIRUNAVUKKARASU

Central Electrochemical Research Institute, Karaikudi 630 006. INDIA

The titled compound is the precussor in the preparation of Triclosan [5-chloro-2-(2,4 Dichloro phenoxy) phenol], an important antibacterial, very much used in cosmetic formulations, is normally obtained by the chemical reduction of 4-chloro-1- (2,4-dichloro phenoxy)-2-nitro benzene using metal/acid or by the catalytic hydrogenation using Raney Nickel catalyst. The synthesis of the titled compound is tried by electrochemical route using titanous/titanic redox couple. The effect of current density, temperature of the electrolysis, the depolariser concentration and the type of the solvent used during the electrolysis are discussed in the paper.

Keywords: Triclosan, redox couple and depolariser.

INTRODUCTION

Triclosan is an important antibacterial, very much used in cosmetic formulations, which is manufactured from 5-Chloro-2-(2,4 dichloro phenoxy)Bezenamine (amino diphenyl ether). The amino diphenyl ether is the reduction product of the corresponding nitro diphenyl ether. Generally the nitro diphenyl ether or any nitro compound is reduced to the corresponding amino compound using metals and acid, preferably iron and hydrochloric acid. For this particular nitro compound iron and acetic acid are used for the reduction and the reaction temperature is maintained at 413-423 K. Amino diphenyl ethers are also manufactured by the catalytic hydrogenation using Raney Nickel [1]. Just to avoid the economical penalties caused by the pollution due to iron sludge, studies were carried out to develop an electrochemical reduction method to reduce the nitro diphenyl ether to the corresponding amino compound. In electrochemical process for the reduction of nitro group to amino group, redox mediators like Zn/Zn^{2+}, Sn/Sn^{2+}, Fe^{2+}/Fe^{3+} and Ti^{3+}/Ti^{4+} [2-7] are generally used in order to avoid the direct reduction of the nitro compound on the electrode surface, which will affect the reduction efficiency due to the formation of resinous product on the electrode surface. The resin formation makes the electrode inactive, resulting in low current efficiency and high cell voltage. In addition to this, side product formation is also taking place. In this paper the results obtained for the electro- synthesis of the titled compound using titanous/titanic redox couple are discussed.

EXPERIMENTAL

All chemicals used in this study are LR grade. One liter glass beaker was used as the cell container and porous pot was used to separate the anolyte and the catholyte. A rotating cylindrical copper electrode deposited with copper was used as the working electrode and lead sheet was used as anode material. The electrolyte was heated using the Sintex heating mantle. Before starting the electrolysis copper was electrodeposited over the cathode surface. After the electrolysis, the electrolyte was cooled to room temperature and the solid residue was filtered to remove the unreacted depolariser. The product was isolated from the electrolyte by neutralising the filtrate with ammonium bicarbonate. The wet product so obtained was dried in vacuum oven.

RESULTS AND DISCUSSION

Table I shows the effect of current density on current efficiency. When the current density is increased from 2.5 A/dm^2 the cell voltage increases from 3.2 V and reaches 7.5 V. The current efficiency gradually falls from 67% and reaches a minimum of 20%. The decrease in current efficiency is due to the hydrogen evolution taking place at the cathode. Further increase in current density results only

TABLE I: Effect of current density on current efficiency

Experimental conditions
Anode : Lead sheet
Cathode : Rotating cylindrical copper deposited copper electrode
Anolyte : 10% (V/V) aqueous sulphuric acid(200 ml)
Catholyte : 15% (V/V) aqueous sulphuric acid(450 ml)
Temperature : 351-353 K
Depolariser concn: 40 gm/lt
Titanous sulphate concn : 1% (Wt/V)
Solvent added to the catholyte : Tetra chloroethylene 125 ml

Current density (A/dm^2)	Cell voltage (V)	Current efficiency (%)
2.5	3.2	67
4.0	3.8	54
6.0	4.3	50
8.0	5.1	42
10.0	7.5	20

in hydrogen evolution reaction. At lower current densities i.e. less than 2.5 A/dm^2 the increase in current efficiency is only minimum, in the order of 0.5-1.0% when the cell is operated at 1.5 A/dm^2. An important observation made during this study is that resin formation on the cathode surface is taking places when the electrolysis conducted at higher current densities i.e. above 4 A/dm^2. This may be due to the depolariser taking part in the electrode reaction and direct reduction of this compound having number of substituents leads to the resin formation. As a result of the resin formation the current efficiency falls gradually with the increase of current density.

TABLE II: Effect of temperature on current efficiency

Experimental conditions
Current density : 2.5 A/dm^2
All other experimental conditions are same as in Table I

Temperature (K)	Cell voltage (V)	Current efficiency (%)
323	5.2	21
333	4.5	35
348	3.7	57
358	3.3	68
373	3.2	63

TABLE III: Effect of depolariser concentration on current efficiency

Experimental conditions
Same as in Table I

Depolariser concn (gm/lit)	Cell voltage (V)	Current efficiency (%)
15	3.2	48
25	3.1	52
40	3.2	67
50	3.8	64
60	4.0	61

As the temperature of the electrolysis is increased, the cell voltage gets reduced and reaches a minimum of 3.2 V at 373 K. The current efficiency increases with the increase of temperature and this increase continues upto 358 K. Further increase in temperature results in current efficiency loss and this is due to the loss of depolariser and solvent because of evaporation. The quality of the product obtained in the experiments conducted at high temperatures i.e. above 373 K is poor and this is due to charring of the product. At 358-373 K the cell voltage is low and the current efficiency is high and the energy consumption falls to a minimum.

Table III shows the effect of depolariser concentration on current efficiency. As the depolariser concentration is increased, current efficiency also increases. The increase of depolariser concentration beyond 40 g/lit. does not result in further increase in current efficiency; but a decline in current efficiency was observed. There is no change in the cell voltage when the depolaiser concentration is maintained between 15-40 g/lit.. Further increase in depolariser concentration results in the increase of cell voltage. This increase in cell voltage is due to the deposit of an organic film on the electrode surface.

TABLE IV: Effect of solvent on current efficiency

Experimental conditions
Current density : 2.5 A/dm^2
All other experimental conditions are same as in Table I except solvent

Solvent	Cell voltage (V)	Current efficiency (%)
Trichloroethylene	3.3	50
Tetrachloroethylene	3.2	67
Toluene	3.3	52

TABLE V: Effect of redox mediator concentration on current efficiency

Experimental conditions

Current density : 2.5 A/dm^2

Solvent : Tetrachloroethylene

All other experimental conditions are same as in Table I

Redox mediator concn (% W/V)	Cell voltage (V)	Current efficiency (%)
0.50	3.4	47
0.75	3.4	51
1.00	3.3	67
1.50	3.3	68
2.00	3.3	70

While studying the effect of solvent added to the electrolyte, it was observed that the solvents used for the studies are not having any effect on the cell voltage, but maximum current efficiency (67%) was obtained in the experiments conducted with terachloroethylene as the solvent.

The increase in the concentration of the redox mediator results in the increase of current efficiency, eventhough there is no effect on the cell voltage. When the redox concentration is increased beyond 2%, the product isolation becomes a difficult one. Hence experiments with higher redox mediator concentration are not carried out.

CONCLUSION

The electrochemical synthesis of the titled compound is possible only at low current densities; the temperature of electrolysis should be maintained at 353-368 K. Tetrachloroethylene is found to be the suitable solvent.

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